

In-situ XAFS observation of Pd-Pt particles supported on various supports – Effect on structure and sulfur tolerance–

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Introduction

Supported Pd-Pt catalysts show high activity for hydrodearomatization (HDA) of diesel fuel which contains sulfur compounds. The activity and selectivity vary with the kinds of supports. The properties of the support like acidity and porosity play an important role in a catalytic reaction, and they should be thoroughly investigated to understand the catalytic properties. In addition to that, it is necessary to know the structure of active metal sites during the reaction, which may change with the kinds of the supports, in order to understand the catalysis completely. In this work, in-situ XAFS (X-ray Absorption Fine Structure) analysis of supported Pd-Pt catalysts was carried out for three kinds of catalysts, and it was found that the kinds of the supports gave significant influence on the structure and sulfur tolerance of metal species

Experimental

Supported Pd-Pt catalysts were prepared by an impregnation method. Silica, alumina, and Ultra stable Y-type zeolite (USY for short, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 13.9$) were used as supports. Total metal content was 1.2 – 2.0 wt% and the atomic ratio of Pd/Pt was 4. The impregnated samples were dried and calcined under O_2 at 573 K for 3 hrs. A round disk of 0.3 g was made from a calcined sample and set in an in-situ XAFS cell [1]. Pd K-edge and Pt L_{III} -edge XAFS spectra were successively measured in-situ during reduction (at 573 K under a flow of 20 % H_2/He at a flow rate of 120 ml/min) and subsequent sulfidation (at 553K under a flow of 100ppm $\text{H}_2\text{S} + 20\% \text{H}_2/\text{He}$ at the flow rate of 120 ml/min) processes. XAFS spectra were observed by a step scanning mode with a data accumulation time of 0.5 – 1 sec for each step. Analysis of the data was conducted with commercially available software (REX, Rigaku Co.). Parameters for curve-fitting analysis were extracted from spectra observed of standard substances at the reaction temperature.

Some of the reactant gases were flammable and toxic. They were removed with absorbers and an exhaust gas burner attached at the end of the reaction system [2].

Results and Discussion

Figure 1 shows Fourier transform of EXAFS ($k^3\chi(k)$) spectra observed for Pd-Pt/ SiO_2 , Pd-Pt/ Al_2O_3 and Pd-Pt/USY after reduction and after sulfidation. Concerning the reduced catalysts, the ratio of coordination numbers of

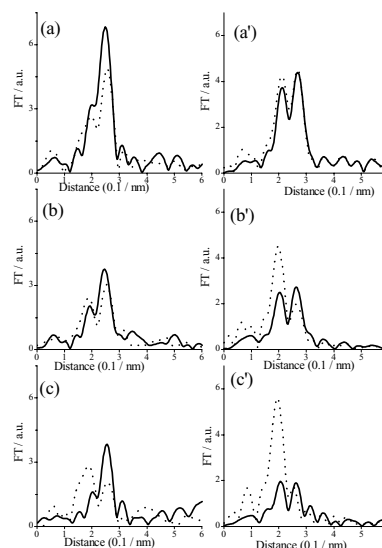


Fig.1 Change in Fourier transform of Pd K (left column) and Pt L_{III} edge EXAFS ($k^3\chi(k)$) after reduction (solid lines) and after sulfidation (dashed lines) observed for Pd-Pt/ SiO_2 ((a) and (a')), Pd-Pt/ Al_2O_3 ((b) and (b')) and Pd-Pt/USY ((c) and (c')).

$\text{CN}(\text{Pt-Pd})/\text{CN}(\text{Pt-Pt})$ was 2.3, 2.7 and 0.97 for Pd-Pt/ SiO_2 , Pd-Pt/ Al_2O_3 , and Pd-Pt/USY, respectively. This value will reach 4 if all the metals are uniformly mixed. Therefore, it is suggested that more uniform Pd-Pt particles were formed on SiO_2 and Al_2O_3 compared with USY. Absolute values of averaged metal-metal coordination numbers of reduced particles were 10.2, 7.5, and 7.3 for Pd-Pt/ SiO_2 , Pd-Pt/ Al_2O_3 , and Pd-Pt/USY, respectively, which indicates that larger particles were formed on SiO_2 compared with Al_2O_3 and USY. Judging from the height of peaks due to metal-sulfur scattering, which appeared at 0.2 nm in both Pd K and Pt L_{III} edge spectra of the sulfided catalysts, the sulfur tolerance of the catalysts is the following order: Pd-Pt/ $\text{SiO}_2 >$ Pd-Pt/ $\text{Al}_2\text{O}_3 >$ Pd-Pt/USY. It is suggested uniformity and the particle size of the metal species have some influence on sulfur tolerance.

References

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